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Published in:
Chemphyschem

DOI:
10.1002/cphc.201100692

Publication date:
2012

CHEMPHYSCHEM

DOI: 10.1002/cphc.201100692

All Organic Host–Guest Crystals Based on a Dumb-Bell-Shaped Conjugated Host for Light Harvesting through Resonant Energy Transfer

Reingard Winkler,[a] Ricarda Berger,[b] Marianna Manca,[c] Jürg Hulliger,*[b] Edwin Weber,[d] Maria A. Loi,*[c] and Chiara Botta*[a]

A feasible way to fabricate functional materials is using supramolecular organization of building blocks.[1,2] Recently, many efforts have been devoted to the assembly of simple photoactive compounds into host–guest systems to provide desired photophysical properties. Among them, the growth of nanochannel forming host–guest systems has received much attention since these systems show a variety of physical properties, including photoactive effects.[3–5] Tuning of photophysical properties, such as the Foerster resonant energy transfers (FRET), has been demonstrated to provide highly efficient materials for energy conversion.[5–9]

An assembly of organic channels provides a system to organize emissive dyes in a host framework, preventing quenching effects but maintaining efficiency for emission at a high dye concentration in the solid state. Photophysical properties of organic channel-forming materials such as perhydrotriphenylene (PHTP) and deoxycholic acid (DCA) have been reported.[7–9] In both systems the main role of the host is to impose a specific geometrical arrangement on the guests and break down intermolecular interactions between them, without interfering with the photoexcitation. However, more intriguing would be to build host–guest systems in which host molecules are able 1) to impose structural organization on the guests and 2) to contribute to the photophysical processes themselves.

With this in mind we prepared an organic channel-forming host material based on 1,8-bis(1)-adamantyl-1,3,5,7-octatetrayene (BAOT). BAOT (Figure 1) is a dumb bell shaped compound, which forms channel-type inclusion compounds when co-crystallized with a number of typical solvent molecules. Adamantyl substituents attached to a tetraalkine spacer build up the walls of parallel channels, wherein linear guest molecules can be inserted by co-crystallization. Co-crystallization of BAOT from 2-butanone yields two types of channels: 1) Oval holes having a maximum cross-section of 9.8 Å and containing guest molecules and 2) smaller ones remaining empty (Figure 1).[10] The inner surface of both channel types consists of adamantane units and ethinyl chain fragments facing each other. Inclusion of the guest molecules diphenylhexatriene (DPH) and quinquethiophene (T5) was established by co-crystallization of dyes and BAOT. We show that by co-inclusion of two dyes into the host, resonant energy transfer occurs among them. Moreover, we observed a contribution of the conjugated host to the photoexcitation pathway of the material.

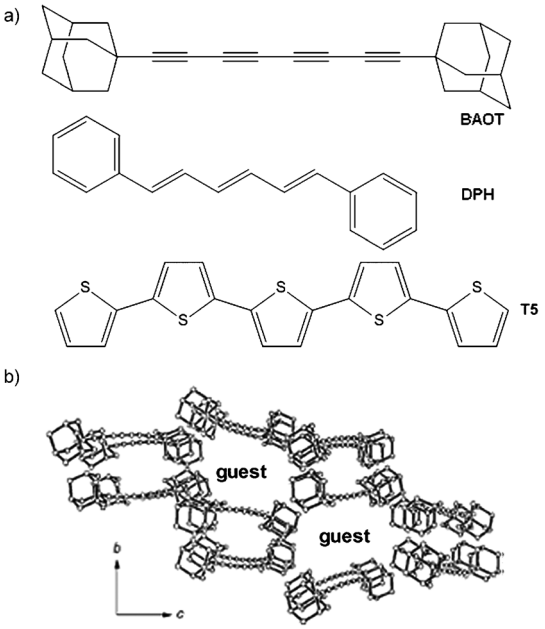

Figure 1. a) Molecular structures of host (BAOT) and guest (DPH, T5) molecules. b) Crystal structure of the host–guest compound viewed along the channels (ref. [10]).

In Figure 2 the fluorescence microscopy image of a T5–BAOT crystal, obtained through slow evaporation from a solution of T5 and BAOT in toluene, shows a well-polarized emission implying a good alignment of the dyes along the crystal axis. In Figure 3 the optical properties of T5, BAOT and the T5–BAOT inclusion compound (IC) are reported. The blue shift in the photoluminescence (PL) spectrum of T5–BAOT (as compared to its solid state) and its similarity with the solution spectrum, are in agreement with the suppression of intermolecular interactions among dyes in the IC. The photoluminescence excitation (PLE) spectra of host–guests based on BAOT

[a] *Dr. R. Winkler, Dr. C. Botta*
Istituto per lo studio delle Macromolecole (ISMAC), CNR
Via Bassini 15, 20133 Milano (Italy)
Fax: (+39) 02.70636400
E-mail: c.botta@ismac.cnr.it

[b] *Dr. R. Berger, Prof. J. Hulliger*
Department of Chemistry and Biochemistry, University of Berne
Freiestrasse 3, 3012 Bern (Switzerland)
Fax: (+41) 31 631-3993
E-mail: juerg.hulliger@iac.unibe.ch

[c] *M. Manca, Prof. Dr. M. A. Loi*
Zernike Institute for Advanced Materials, University of Groningen
Nijenborgh 4, 9747 AG Groningen (The Netherlands)
E-mail: M.A.Loi@rug.nl

[d] *Prof. E. Weber*
Institute of Organic Chemistry, TU Bergakademie Freiberg
Leipziger Strasse 29, 09596 Freiberg/Sachsen (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201100692.

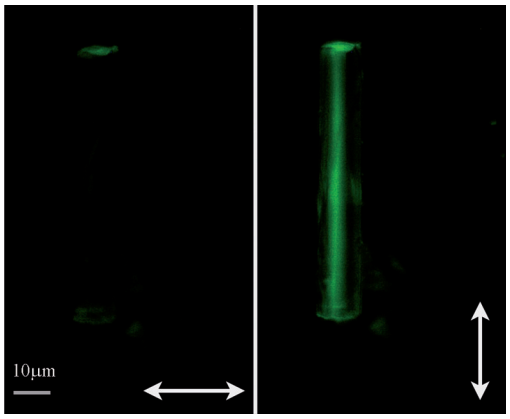

Figure 2. Polarized fluorescence microscopy image of a T5–BAOT crystal (the arrows show the polarization axis).

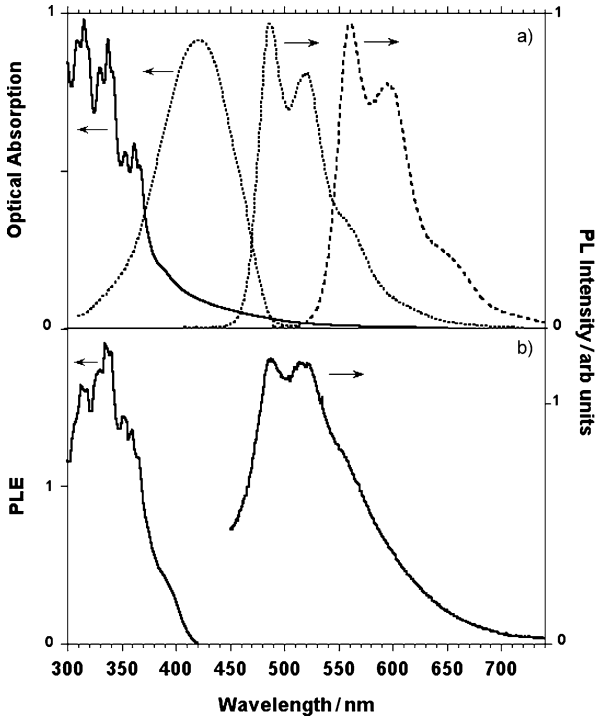

Figure 3. a) Absorption spectra of T5 (•••••) and BAOT (——) in toluene. PL spectra of T5 in toluene (•••••) and T5 powders (-----) excited at 400 nm. b) PLE spectrum (emission at 530 nm) and PL spectrum (excited at 400 nm) of T5–BOAT.

provide information about the photoexcitation pathways of BAOT inclusion compounds. As seen in Figure 3 the PLE of T5–BAOT shows the sharp peaks of the absorption spectrum of BAOT, indicating that the host contributes to the excitation of the guest molecule. Similar results are obtained for the DPH–BAOT system (see Figure S1 in the Supporting Information). The PL quantum yields (QY) of T5 in solution and in the solid state are summarized in Table 1. It is known that the PL QY of T5, as also for other thiophene aggregates, is low due to the strong intermolecular interactions that quench the emission in the solid state.[11] On the other hand, the T5–BAOT shows an

Table 1. PL QY and lifetimes of T5 in solution, as a powder aggregate, included in BAOT and co-included in BAOT with DPH.[a]

	PL QY [%]	Lifetime [ns]
T5 solution	32[b]	0.8[b]
T5 powder	2	1
T5–BAOT	11	0.4
DPH/T5–BAOT[c]	18	1.5

[a] Excitation wavelength 360 nm. [b] Ref. [13]. [c] DPH/T5 90:10.

enhancement of the QY with respect to the aggregate state, although its value is nevertheless lower than in solution. This latter fact is not related to interactions of T5 with host molecules (see Figure S2 in the Supporting Information), but might rather be due to the formation of complexes of thiophene with some oxygen molecules entrapped into the host during the photoexcitation processes, as recently reported for PHTP-based thiophene ICs.[12] T5–T5 resonant homo-transfer processes would then increase the efficiency of these few quenching sites,[6,7,9] leading to a reduced PL QY of the crystal.

The inclusion of two dyes (featuring suited optical properties) into a host crystal, providing an interchannel distance of about 1 nm, has been proven to produce nanostructures for efficient energy conversion both for inorganic[5,6] and organic[7–9] hosts. With the aim of exploiting the peculiar BAOT properties for energy harvesting in the UV range, we co-included DPH and T5 into the BAOT system and studied the emission properties for different relative concentrations of the dyes. The two dyes were chosen because they bring in matching optical properties for FRET from DPH (donor) to T5 (acceptor).[8,9] In Figure 4 the PL and PLE spectra of co-ICs for different DPH/T5 molar ratios (100:0, 99:1; 95:5; 90:10) are reported. The PL

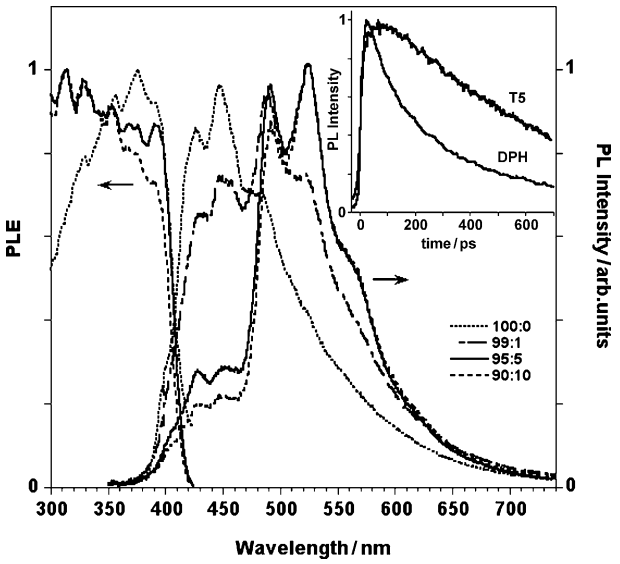

Figure 4. Normalized PL and PLE spectra of DPH/T5–BOAT at different DPH/T5 molar concentrations (95:5, 90:10, emission at 530 nm and 100:0, emission at 445 nm), PL excitation is at 350 nm. Inset: PL decay of DPH/T5–BOAT (90:10) measured for the 400–440 nm (DPH) and 560–600 nm (T5) spectral regions, excitation at 360 nm.

spectra demonstrate that FRET from DPH to T5 occurs in the BAOT host through the fact that for a DPH/T5 ratio of 99:1 the emission of the two dyes shows similar intensity,[14] whereas no emission is detected from T5 upon dissolution of the host–guest system in a common solvent (see Figure S3 in the Supporting Information). The PL intensity of the T5 emission shows an increase during the first 50 ps, which is in agreement with a quick transfer of energy from DPH to T5 (see insert Figure 4). The longer lifetime of the T5 emission in the co-IC is consistent with the long lifetime of the DPH donor.[9] Finally, the presence of BAOT peaks in the PLE spectra of the co-IC (Figures 4 and S4 in the Supporting Information) demonstrates that the host contributes to the photoexcitation of guests, thus increasing the light harvesting properties of the co-IC in the UV region. We stress the fact that the use of BAOT as a host for energy conversion allows us to reach full light harvesting with only two dyes, without the need of a third UV absorbing guest molecule, which is necessary in inorganic hosts[5,6] or non-conjugated organic hosts[8,9] reported so far, in order to convert energy from the UV region into visible light.

In conclusion, we prepared a novel, fully organic nanostructured host–guest material based on a conjugated host, BAOT, and we showed that this host is able to harvest light in the UV region. The co-inclusion of two dyes, DPH and T5, possessing suitable optical properties for FRET processes, provides organic host–guest systems with a broad emission in the visible range and UV light harvesting through the host. The development of such host–guest systems, designed for optical energy harvesting, may once allow to produce efficient energy converters made of all-organic materials.

Experimental Section

BAOT was prepared as reported elsewhere.[10] T5 and DPH were purchased from Aldrich. Inclusion of the guest molecules DPH and T5 was established by co-crystallization of dyes and BAOT using 2-butanone with a host/guest ratio of about 3:1. PL continuous wave measurements were obtained with a SPEX 270 M monochromator equipped with a N_2 cooled charge-coupled device, exciting with a monochromated Xe lamp. The spectra were corrected for the instrument response. PL QY on solid-state materials were measured with a home-made integrating sphere and reported elsewhere.[8a] Microscopy fluorescence images were collected with a Nikon Eclipse TE2000-U inverted confocal microscope, exciting with a 100W Hg lamp equipped with a 330–380 nm band-pass excitation filter. For polarized measurements, a rotating polarizer was placed between the sample and the detector. The time-resolved PL measurements of the samples were excited by a 150 fs pulsed Kerr-mode-locked Ti-sapphire laser, frequency-doubled at about 360 nm, and the steady-state PL emissions were measured by a Hamamatsu streak camera working in synchroscan mode. All measurements were performed at room temperature and the spectra were calibrated for the instrumental response.

Acknowledgements

This work was partially supported by the European Commission-through the Human Potential Program RTN 'Nanomatch' Contract No. MRTN-CT-2006–035884 and by Progetto Cariplo SOLCO.

Keywords: host–guest · inclusion compounds · light harvesting · resonant energy transfer · self-assembly

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[14] The fact that for a T5 concentration as high as 10% a weak DPH emission is observed indicates that FRET towards T5 is not complete due to the presence of solvent molecules that prevent a complete filling of the channels with the guests and due to a possible inhomogeneous distribution of the two guest species into the host.

Received: September 8, 2011
Revised: October 10, 2011
Published online on November 14, 2011

